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(54) Title: COBALT-BASED CATALYSTS AND PROCESS FOR PRODUCING SYNTHESIS GAS

(57) Abstract: A process is disclosed for the catalytic partial oxidation of light hydrocarbons such as methane. The process involves the conversion of a hydrocarbon feedstock by contacting a feed stream comprising the hydrocarbon feedstock and an oxygen-containing gas with a catalyst in a reaction zone maintained at conversion-promoting conditions in a millisecond contact time reactor effective to produce an effluent stream containing primarily carbon monoxide and hydrogen. Certain preferred catalysts of the invention comprise cobalt metal and/or cobalt containing compound(s), a promoter, and a refractory support are capable of efficiently producing syngas at high selectivities for CO and H₂ products.

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COBALT-BASED CATALYSTS AND PROCESS FOR PRODUCING SYNTHESIS GAS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application No. 60/165,981 filed November 17, 1999.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention generally relates to catalysts and processes for converting a light hydrocarbon (e.g., natural gas) and oxygen to a product containing a mixture of carbon monoxide and hydrogen, also referred to as synthesis gas or syngas. More particularly, the invention relates to supported cobalt-containing catalysts and syngas production processes employing them.

Description of Related Art

Large quantities of methane, the main component of natural gas, are available in many areas of the world, and natural gas is predicted to outlast oil reserves by a significant margin. However, most natural gas is situated in areas that are geographically remote from population and industrial centers. The costs of compression, transportation, and storage make its use economically unattractive. To improve the economics of natural gas use, much research has focused on methane as a starting material for the production of higher hydrocarbons and hydrocarbon liquids. The conversion of methane to hydrocarbons is typically carried out in two steps. In the first step, methane is reformed with water to produce carbon monoxide and hydrogen (i.e., synthesis gas or syngas). In a second step, the syngas is converted to hydrocarbons, for example, using the Fischer-Tropsch process to provide fuels that boil in the middle distillate range, such as kerosene and diesel fuel, and hydrocarbon waxes.

Current industrial use of methane as a chemical feedstock proceeds by the initial conversion of methane to carbon monoxide and hydrogen by either steam reforming, which is the most widespread process, or by dry reforming. Steam reforming is the major process used commercially for the conversion of methane to synthesis gas, the conversion proceeding by the strongly endothermic reaction shown in Equation 1.



This process requires the input of appreciable quantities of thermal energy to initiate and maintain the reaction. Although steam reforming has been widely practiced for over five decades, efforts to improve the energy efficiency and reduce the capital investment required for this technology continue.

5 In contrast, the partial oxidation of methane and other light hydrocarbons is exothermic, and under ideal conditions can proceed according to the stoichiometry of Equation 2 to yield a syngas mixture with a H₂:CO ratio of 2:1. This ratio is more useful than the H₂:CO ratio from steam reforming for such downstream operations as the conversion of the syngas to chemicals such as methanol and to fuels.



Another advantage of utilizing partial oxidation processes for syngas production is that oxidation reactions are typically much faster than reforming reactions, and therefore, allow the use of much smaller reactors.

The non-catalytic partial oxidation of methane carried out at high temperatures (≥1300°C) and high pressures (150 atm) can produce syngas at high selectivities for CO and H₂ products (Chang et al. 1993 *Catalysis Letters* 21:215-224). While currently limited as an industrial process due to the technical difficulties of obtaining the desired stoichiometry, partial oxidation offers an additional advantage over conventional steam reforming of methane in that significant heat is released by the oxidation reaction, thereby eliminating the need for a fuel gas. Depending on the relative proportions of hydrocarbon and oxygen and other reaction conditions, other, more highly exothermic partial oxidation reaction stoichiometries, can occur instead of or in addition to the reaction stoichiometry shown in Equation 2. However, the greater amounts of heat produced by those reactions, if excessive, can damage the reactor or its components.

25 In order to avoid such extreme conditions, various metal-containing catalysts have been employed to catalyze the partial oxidation of hydrocarbons such as methane. In a typical catalytic partial oxidation process, the light hydrocarbon is mixed with air, oxygen-enriched air, or oxygen, and introduced to a catalyst at elevated temperature and pressure. The selectivities of catalytic partial oxidation to the desired products (i.e., carbon monoxide and hydrogen) are controlled by several factors. One of the most important of these factors is the choice of catalyst composition. Choosing an economical catalyst that is efficient and provides excellent selectivities for CO and H₂ is a problem. Typically, catalyst compositions have included precious metals and/or rare earths. The large volumes of expensive catalysts

required in most conventional catalytic partial oxidation processes have placed these processes generally outside the limits of economic justification.

For successful operation at commercial scale, the catalytic partial oxidation process must be able to achieve a high conversion of the methane feedstock at high gas hourly space velocities, and the selectivity of the process to the desired products of carbon monoxide and hydrogen must be high. Such high conversion and selectivity must be achieved without detrimental effects to the catalyst, such as the formation of carbon deposits ("coke") on the catalyst, which severely reduces catalyst performance. Accordingly, substantial effort has also been devoted in the art to the development of catalysts allowing sustainable commercial performance without coke formation.

A number of process regimes have been proposed for the production of syngas via catalyzed partial oxidation reactions, and a number of catalyst formulations have been examined. For example, European Pat. No. EP303438 describes one method for the catalytic partial oxidation of methane using a high temperature, high pressure mixture of methane and oxygen at GHSV (gas hourly space velocity) of up to 5×10^5 . U.S. Pat. No. 5,149,464 discloses a method for selectively converting methane to syngas at 650°C to 950°C by contacting the methane/oxygen mixture with a solid catalyst comprising a supported d-Block transition metal, transition metal oxide, or a compound of the formula $M_xM'_yO_z$ wherein M' is a d-Block transition metal and M is Mg, B, Al, Ga, Si, Ti, Zr, Hf or a lanthanide. U.S. Pat. No. 5,500,149 discloses various transition metals that can act as catalysts in the reaction $CO_2 + CH_4 \rightarrow 2CO + 2H_2$, and demonstrates how reaction conditions can affect the product yield.

The partial oxidation of methane to synthesis gas using various transition metal catalysts under a range of conditions has been described by Vernon, D.F. et al. (*Catalysis Letters* 6:181-186 (1990)). European Pat. App. Pub. No. 640561 discloses a catalyst for the catalytic partial oxidation of hydrocarbons comprising a Group VIII metal on a refractory oxide having at least two cations. U.S. Pat. No. 5,149,516 discloses a process for partial oxidation of methane to produce a product including carbon monoxide and hydrogen employing a type of perovskite catalyst, such as $LaCoO_3$. U.S. Pat. No. 5,447,705 discloses another catalyst having a perovskite crystalline structure and the general composition: $Ln_xA_{1-y}B_yO_3$, wherein Ln is a lanthanide and A and B are different metals chosen from Group IVb, Vb, VIb, VIIb or VIII of the Periodic Table of the Elements. Lago et al. (1997 *J. Catalysis* 167:198-209; and in Grasselli, et al. (eds.) 3rd World Congress on Oxidation Catalysis,

Elsevier Science B.V., 1997, pp. 721-730) also describe certain perovskite catalyst precursors containing cobalt and lanthanide oxides for the partial oxidation of methane to synthesis gas.

U.S. Pat. No. 5,338,488 describes a process for the production of synthesis gas by oxidative conversion of methane using composite catalysts containing certain transitional and alkaline earth metal oxides. The transition metals include Ni, Co, Pd, Ru, Rh, Ir and mixtures thereof; and the alkaline earth metals include Mg, Ca, Ba, Sr and mixtures thereof. U.S. Pat. No. 5,368,835, U.S. Pat. No. 5,411, 927 and U.S. Pat. No. 5,756,421 describe the oxidative conversion of methane to synthesis gas using catalysts containing certain transition and non-transition metal oxides.

Some investigators have examined certain cobalt-containing catalysts, many of which also include nickel or a Group VIII metal. For example, U.S. Pat. No. 5,752,995 describes a cobalt promoted nickel catalyst for the production of gases rich in H from methane with decreased carbon deposition. The catalyst may include certain refractory materials as supports for the catalyst. Xianjun et al. (1998 "Microwave Effect on Partial Oxidation of Methane to Syngas over Co/La₂O₃" *Chinese Journal of Chemical Physics* 11:193-196) describe a Co/La₂O₃ catalyst and activation of the reaction by microwave heating. However, Xianjun et al. (1999 "Partial Oxidation of Methane to Syngas by Microwave Initiating" *Chinese Journal of Catalysis* 20:73-75) found that the activity and selectivity of a Co/La₂O₃ catalyst decreased markedly with increasing time on-stream. U.S. Pat. No. 5,235,804 suggests that certain cobalt oxide catalysts are capable of partially oxidizing C₁₋₂₀ hydrocarbons and controlling NO_x and other pollutant emissions associated with the combustion of hydrocarbon fuels. These catalysts may be supported on alumina or similar substrate, or in the form of granules, extrudates, coating on a metal heat exchanger surface, metal honeycomb or ceramic honeycomb. Chinese Pat. No. 1130150A discloses a cobalt-alkaline earth-lanthanide-containing catalyst used to convert CH₄ to CO and H₂ at 300-900°C. Japanese Pat. No. 1-52055 describes a cobalt-alumina-magnesia spinel catalyst and a cobalt oxide-barium aluminate catalyst for catalyzing the partial oxidation of hydrocarbons. Others have employed certain cobalt-containing catalysts in hydrocarbon reforming processes. For example, U.S. Pat. No. 4,024,075 (Russ et al.) describes a supported cobalt catalyst for reforming hydrocarbons with steam and carbon dioxide. Wang, et al. (1998 *Chinese J. of Catalysis* 19:196-200) disclose certain reforming catalysts containing Co/Al₂O₃ for methane and carbon dioxide reformation to syngas.

U.S. Patent No. 5,989,457 describes a process for making synthesis gas by methane reforming with carbon dioxide using a Co, Ni, Pt or Pd catalyst on a thermally stabilized

oxidic support containing an oxide of Y, La, Al, Ca, Ce or Si. U.S. Patent No. 6,060,420 describes a catalyst for purifying exhaust gas comprising an alumina or zirconia catalyst carrier substrate and a composite oxide of A-site defect perovskite structure represented by the general formula: $A_{1-\alpha}BO_{3-\delta}$ where A is an alkali metal, alkaline earth metal, rare earth element, Y or Pb. B is Mn, Co, Ti, Fe, Ni, Cu and Al and α is from 0.12-0.15 and δ is up to 1.

One disadvantage of many of the existing catalytic hydrocarbon conversion methods is the need to include steam in the feed mixture to suppress coke formation on the catalyst. Another drawback of some of the existing processes is that the catalysts that are employed often result in the production of significant quantities of carbon dioxide, steam, and C_2+ hydrocarbons. Also, large volumes of catalyst are sometimes required, necessitating the use of exceptional devices in an attempt to evenly distribute the feed to the top of the catalyst bed. None of the existing processes or catalysts are capable of providing high conversion of reactant gas and high selectivity of CO and H_2 reaction products. Accordingly, there is a continuing need for better processes for the catalytic partial oxidation of light hydrocarbons, in which the catalyst retains a higher level of activity and selectivity to carbon monoxide and hydrogen under conditions of high gas space velocity and elevated pressure.

SUMMARY OF THE INVENTION

The present invention provides processes for preparing synthesis gas using cobalt-containing catalysts for the catalytic partial oxidation of any gaseous hydrocarbon having a low boiling point (e.g. C_1 - C_5 hydrocarbons, particularly methane, or methane containing feeds). One advantage of the cobalt catalysts of the process is that they retain a high level of activity and selectivity to carbon monoxide and hydrogen under conditions of high gas space velocity and elevated pressure. Another advantage of the new catalytic processes is that they are economically feasible for use in commercial-scale conditions.

Also provided by the present invention are supported cobalt-containing catalysts for catalyzing the partial oxidation of a hydrocarbon, and their methods of making. The supported catalysts contain cobalt metal and/or one or more cobalt containing compound(s) including the various oxides of cobalt, cobalt containing spinels, mixed metal oxides or metals of cobalt with magnesia, nickel, $LaZrO_2$, lanthanum oxide, alumina, zirconia, ceria, and calcium oxide. The spinels and mixed metal oxides include $CoAl_2O_4$, $MgCo_2O_4$, Co_2AlO_4 , $LaAl_8Co_2O_{13}$, $CaCo_2O_4$, $ZnCo_2O_4$, and $NiCo_2O_4$. The catalyst may be comprised of a cobalt-containing hydrotalcite, including the hydrotalcite $Co_6Al_2(OH)_{16}CO_3 \cdot 4 H_2O$. Preferably, the support structure comprises a spinel, a perovskite, magnesium oxide, a

hydrotalcite, LaZrO_2 , lanthanum oxide, a pyrochlore, a brownmillerite, zirconium phosphate, magnesium stabilized zirconia, zirconia stabilized alumina, silicon carbide, yttrium stabilized zirconia, calcium stabilized zirconia, yttrium aluminum garnet, alumina, cordierite, ZrO_2 , ZnO , LaAlO_3 , MgAl_2O_4 , SiO_2 or TiO_2 . The cobalt metal and/or cobalt containing compound(s) are disposed on or within the support structure. In some of the more preferred 5 embodiments, the catalyst support structure is a hydrotalcite, spinel, a perovskite, a pyrochlore or a brownmillerite, and the cobalt metal and/or cobalt containing compound(s) are incorporated into the support structure.

10 In certain embodiments of the catalysts the support structure comprises a refractory oxide, which may be in the form of a foam structure. Preferably such a foam structure comprises about 12-60 pores per centimeter of structure. Alternatively, in some embodiments the support structure is in the form of a honeycomb monolith structure.

15 In some embodiments, the catalyst comprises the cobalt metal and/or cobalt containing compound(s) on a support structure comprising Al_2O_3 . Some embodiments comprise a Co containing hydrotalcite. In some embodiments the catalyst comprises mixtures of cobalt metal and/or oxides with magnesia in the form of solid solution. Another catalyst embodiment comprises cobalt spinels and mixed metal oxides including CoAl_2O_4 , MgCo_2O_4 , Co_2AlO_4 , $\text{LaAl}_8\text{Co}_2\text{O}_3$, CaCo_2O_4 , ZnCo_2O_4 , and NiCo_2O_4 . And others comprise cobalt metal and/or oxides on LaZrO_2 , alumina, lanthanum oxide, and zirconia.

20 In some embodiments a syngas catalyst device is provided that comprises cobalt metal and/or cobalt oxide, a promoter chosen from the group consisting of Mn, Ni, La, Cu, Sm, Yb, Eu, Pr, Ce, Y, Pt, Rh and Re, and a support structure comprising partially stabilized zirconia. In some embodiments the catalyst device comprises cobalt metal and/or cobalt oxide, manganese metal and/or manganese oxide, magnesium oxide and a partially stabilized 25 zirconia support. In some embodiments the catalyst comprises 0.15 wt% Pt, about 6.5 wt% Co and about 6.1 wt% Mg by catalyst weight.

30 In certain embodiments a syngas catalyst is prepared by impregnating a refractory metal oxide support, such as a PSZ foam, with a solution of an oxidizable magnesium salt and then calcining the resulting magnesium impregnated support. The magnesium impregnated support is then re-impregnated with a solution of an oxidizable cobalt salt to provide a cobalt/magnesium oxide intermediate, which is then calcined and reduced. In certain preferred embodiments, this (cobalt/magnesium) oxide loaded support is then coated with a promoter by impregnating with a solution of an oxidizable metal salt, such as a nitrate or an acetate. Suitable promoter metals include Mn, Ni, La, Cu, Sm, Yb, Eu, Pr, Ce, Y, Pt,

Rh and Re. The promoter/(cobalt/magnesium) oxide coated support is then calcined and reduced to provide a supported catalyst that is active for catalyzing the net partial oxidation of methane in the presence of O₂ to CO and H₂ under partial oxidation promoting conditions in a short contact time reactor.

5 Also provided by the present invention is a process for the net partial oxidization of a C₁-C₅ hydrocarbon to form a product gas mixture comprising CO and H₂. According to certain embodiments, the process comprises passing a reactant gas mixture comprising a C₁-C₅ hydrocarbon and an O₂-containing gas over a supported catalyst, or catalyst device, as described above, in a millisecond contact time reactor. The contact time of a portion of
10 reactant gas mixture in contact with the catalyst device does not exceed about 10 milliseconds. The process also includes maintaining net catalytic partial oxidation promoting conditions during operation of the reactor. Such reaction-promoting conditions include maintaining a favorable hydrocarbon:oxygen molar ratio in the reactant gas mixture, maintaining a favorable catalyst temperature, maintaining a favorable reactant gas preheat
15 temperature and reactant flow rate. In certain preferred embodiments the process includes maintaining the reactant gas mixture and the catalyst at a temperature of about 600-1,200°C during contact. In some embodiments the temperature is maintained at about 700-1,100°C.

In certain embodiments of the process, maintaining net catalytic partial oxidation promoting conditions includes mixing a methane-containing feedstock and an oxygen-
20 containing feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen molar ratio of about 1.25:1 to about 3.3:1. In some of these embodiments, the mixing step is such that it yields a reactant gas mixture feed having a carbon:oxygen ratio of about 1.3:1 to about 2.2:1, or preferably about 1.5:1 to about 2.2:1. In some of the most preferred
25 embodiments the mixing step provides a reactant gas mixture feed having a carbon:oxygen ratio of about 2:1.

In some embodiments of the process the oxygen-containing gas that is mixed with the hydrocarbon also contains steam or CO₂, or both. In some embodiments of the process the C₁-C₅ hydrocarbon comprises at least about 50 % methane by volume, and in some of the preferred embodiments the C₁-C₅ hydrocarbon comprises at least about 80 % methane by
30 volume.

Some embodiments of the process include preheating the reactant gas mixture, to facilitate catalyst activation for the reaction. Some embodiments of the processes comprise passing the reactant gas mixture over the catalyst at a space velocity of about 20,000 to about

100,000,000 normal liters of gas per kilogram of catalyst per hour (NL/kg/h). In certain of these embodiments, the gas mixture is passed over the catalyst at a space velocity of about 50,000 to about 50,000,000 NL/kg/h. In some embodiments of the reactor is operated at a pressure of about 100-12,500 kPa during the contacting, and in some of the more preferred
5 embodiments the pressure is maintained at about 130-10,000 kPa. These and other embodiments, features and advantages of the present invention will become apparent with reference to the following description.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Supported catalysts, or catalyst devices, useful for catalytically converting C₁-C₅
10 hydrocarbons to CO and H₂ contain cobalt metal and/or cobalt-containing compound(s) have been developed which include support materials such as hydrotalcites, spinels, perovskites, magnesium oxide, lanthanum oxide, LaZrO₂, pyrochlores, brownmillerites, zirconium phosphate, magnesium stabilized zirconia, zirconia stabilized alumina, silicon carbide, yttrium stabilized zirconia, calcium stabilized zirconia, yttrium aluminum garnet, alumina,
15 cordierite, mullite, ZrO₂, ZnO, LaAlO₃, MgAl₂O₄, SiO₂ or TiO₂. In some of these catalysts, the cobalt metal and/or cobalt-containing compound(s) are incorporated into the structure of a hydrotalcite, spinel, perovskite, pyrochlore or brownmillerite. As described in the following examples, representative catalysts comprised of cobalt metal and/or one or more cobalt-containing compounds are prepared utilizing conventional techniques such as impregnation,
20 wash coating, adsorption, ion exchange, precipitation, co-precipitation, deposition precipitation, sol-gel method, slurry dip-coating, microwave heating, and the like, all of which are well known in the field. Preferred techniques are wash coating, impregnation, sol-gel methods and co-precipitation. As described in more detail below, some of the more active supported catalysts include a promoter and are prepared using a multi-step support
25 loading process and defined calcining and reducing program.

In some cases, the catalyst components with or without a ceramic support material are extruded to prepare a three-dimensional form or structure such as a honeycomb, foam, or other suitable tortuous-path structure. The catalyst components may be added to the powdered ceramic composition and then extruded to prepare the foam or honeycomb. A
30 suitable foam catalyst structure has from 30 to 150 pores per inch (12 to 60 pores per centimeter). Alternative forms for the catalyst include refractory oxide honeycomb monolith structures, or other configurations having longitudinal channels or passageways permitting high space velocities with a minimal pressure drop. Such configurations and their manner of making are described, for example, in *Structured Catalysts and Reactors*, A. Cybulski and

J.A. Moulijn (Eds.), Marcel Dekker, Inc., 1998, p. 599-615 (Ch. 21, X. Xu and J.A. Moulijn, "Transformation of a Structured Carrier into Structured Catalyst").

EXAMPLES

Catalyst Preparation

5 Exemplary catalysts were prepared as described below, and were tested for their activity in catalyzing the production of synthesis gas in a short contact time, or millisecond contact time reactor similar to that described by L.D. Schmidt and his colleagues at the University of Minnesota in U.S. Pat. No. 5,648,582 and in *J. Catalysis* 138, 267-282 (1992) for use in the production of synthesis gas by direct oxidation of methane over a catalyst such
10 as platinum or rhodium. The disclosures of those references are incorporated herein by reference. The samples obtained from the following examples were evaluated at defined high gas hourly space velocities, temperature and pressure and the levels of CH₄ and O₂ conversion and selectivities to CO and H₂ products were determined.

Example 1: Co/Mg/O (Co:Mg = 1.2)

15 In a 4 L glass beaker was mixed 211.2 g Co(NO₃)₂·6H₂O and 371.8 g of Mg(NO₃)₂·6H₂O in 2332.2 g of H₂O. To this mixture was added 340 mL of 20% NH₄OH solution. The mixture was stirred for 90 minutes and then allowed to settle overnight. Solids were collected by centrifuge and then washed with deionized water. After drying at 110°C overnight, the solids were then ground to powder and calcined in air at 600°C for 2 hours.
20 This procedure was repeated five times and products were combined. Powder X-ray diffraction analysis indicated spinel-like phase formation and MgO. For the purposes of the present disclosure the term "spinel-like" refers to a mixed metal oxide that conforms to the molecular formula AB₂O₄, where A and B represent the two metals forming the mixed metal oxide. Chemical analysis by inductively coupled plasma spectrometry gave 51.95% Co and
25 17.2%Mg.

Example 2: Co/Mg/O (Co:Mg = 1)

In a 4 L glass beaker was mixed 162.37 g Co(NO₃)₂·6H₂O and 285.97 g of Mg(NO₃)₂·6H₂O in 1794 g of H₂O. To this mixture was added 285 mL of 20% NH₄OH solution. The mixture was stirred for 60 minutes and then allowed to settle overnight. Solids
30 were collected by centrifuge and then washed with deionized water. After drying at 110°C overnight, the solids were then ground to powder and calcined in flowing nitrogen at 550°C for 6 hours. Powder X-ray diffraction analysis indicated spinel-like phase formation and

MgO. Chemical analysis by inductively coupled plasma spectrometry gave 32.20% Co and 12.80%

Example 3: Co/Al/O (Co:Al = 0.4)

5 In a 2 L Roto-Vap flask was mixed, 145.51 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 375.10 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1000 mL H_2O . After water removal, the sample was melted out of the flask, poured into a crystallizing dish and then calcined in air at 400°C for two hours. Powder X-ray diffraction analysis indicated spinel-like phase formation. Chemical analysis by inductively coupled plasma spectrometry gave 26.8% Co and 29.0% Al.

Example 4: Co/Mg/O (Co:Mg = 2)

10 In a 2 L Roto-Vap flask, 291.04 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 128.20 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1000 mL H_2O was mixed together. After water removal, the sample was melted out of the flask, poured into a crystallizing dish and then calcined in air at 400°C for two hours. Powder X-ray diffraction analysis indicated a spinel-like phase formation and MgO. Chemical analysis by inductively coupled plasma spectrometry gave 51.5% Co and 11.4%
15 Mg.

Example 5: Co-Al-Substituted hydrotalcite

Added a solution containing 10.5 kg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 6.77 kg $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 50.52 kg H_2O to one containing 10.10 kg NaOH (50%), Na_2CO_3 and 36.08 kg H_2O slowly over a 4 hour period maintaining the mixture at 35°C. After the addition, the container was
20 held at 35 °C for 30 minutes, then raised to 65°C and held for 18 hours after which the container was cooled to room temperature. The mixture was filtered, washed and dried at 85°C in a vacuum oven with nitrogen purge. Powder X-ray diffraction analysis showed the presence of $\text{Co}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. Chemical analysis by inductively coupled plasma spectrometry gave 38.2% Co, 7.48% Al, and 0.72% Na.

25 **Example 6: Co/Al/O (Co:Al = 1.7)**

In a 2 L Roto-Vap flask was mixed, 291.04 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 187.60 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1000 mL H_2O . After water removal, the sample was melted out of the flask, poured into a crystallizing dish and then calcined in air at 400°C for two hours. Powder X-ray diffraction analysis indicated spinel-like phase formation. Chemical analysis
30 by inductively coupled plasma spectrometry gave 50.0% Co and 13.7% Al.

Example 7: Co/Mg/O (Co:Mg = 3)

A solution containing 84.2 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 mL H_2O was added to 92.03 g of Co_3O_4 (Alfa, Lot Number A24F29). The mixture was heated in air at $60^\circ\text{C}/\text{hour}$ to 400°C and held for 2 hours at 400°C . The resulting material was calcined in air at 600°C for 2 hours. Powder X-ray diffraction analysis indicated spinel-like phase formation and MgO . Chemical analysis by inductively coupled plasma spectrometry gave 59.5% Co and 8.01% Mg.

Example 8: CoAl_2O_4

A sample was obtained from Alfa Aesar (Lot Number B05J32). X-ray diffraction analysis showed the presence of CoAl_2O_4 .

Example 9: Co/Ni/Na/Al/O

In a 3 L round bottom flask, a mixture containing 140 g NaOH , 50 g Na_2CO_3 and 500 mL H_2O was added dropwise over a 4.2 hour period to one containing 145.52 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 145.52 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 93.75 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 700 mL H_2O with stirring. The resulting mixture was heated at 65°C for 18 hours. After cooling, solids were recovered by centrifugation, washed with H_2O , and dried at 110°C overnight. The dried solids were ground and then calcined in air by heating $60^\circ\text{C}/\text{h}$ to 550°C , holding at 550°C for 10 hours. Powder X-ray diffraction analysis indicated spinel-like phase formation as a primary phase. Chemical analysis by inductively coupled plasma spectrometry gave 25.4% Co, 28.4% Ni, 5.84% Al, and 7.02% Na.

Example 10: Co/La/Zr/O

31.5 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 500 ml water. 100 g of La-doped zirconium hydroxide (MEI XZO 681/01) was added and stirred for 1 hour. The slurry was filtered without washing. The solid was dried at 135°C , and then pressed into pellets. The pellets were heated 4 hours at 600°C , and then crushed into 6-16 mesh granules. Chemical analysis by inductively coupled plasma spectrometry gave 2.87% Co, 3.06% La, and 59.6% Zr.

Example 11: Co/La/Al/O

In a Roto-Vap flask was mixed, 500 mL 1M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 200 mL 1M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 100 mL 1 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The mixture was evaporated to 200 mL, poured into a crucible and dried at 110°C in a vacuum oven for 6 days. The resulting material was calcined at 325°C for 24 hours, ground to a powder, and then calcined at 1000°C for 96 hours.

Example 12: Co/Ca/O

In a 2 L Roto-Vap flask was mixed, 291.04 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 118.08 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 1000 mL H_2O . After water removal, the sample was melted out of the flask, poured into a crystallizing dish and then calcined in air at 400°C for two hours. Powder X-ray diffraction analysis indicated spinel-like phase formation. Chemical analysis by inductively coupled plasma spectrometry gave 30.4% Co and 12.8% Ca.

Example 13: Co/La/Al/O

In a Roto-Vap flask was mixed, 500 mL 1M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 200 mL 1M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 100 mL 1 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The mixture was evaporated to 200 mL, poured into a crucible and dried at 110°C in a vacuum oven for 6 days. The resulting material (123.75 g) was calcined at 325°C for 24 hours, ground to a powder, and then calcined at 900°C for 96 hours. Chemical analysis by inductively coupled plasma spectrometry gave 6.33% Co, 45.0% La, and 5.42% Al.

Example 14: 2%Co/Al₂O₃

8.47 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 184 mL H_2O . 105 g gamma-alumina (dried at 110°C overnight) were added with stirring to the CoCl_2 solution. The water was evaporated off by heating on a hot plate at approximately 90°C. The catalyst was stirred every 10 to 15 minutes until dry.

Example 15: Co/Zn/O

In a 2 L Roto-Vap flask was mixed, 291.04 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 148.74 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1000 mL H_2O . After water removal, the sample was melted out of the flask, poured into a crystallizing dish and then calcined in air at 400°C for two hours. Powder X-ray diffraction analysis indicated spinel-like phase formation and ZnO. Chemical analysis by inductively coupled plasma spectrometry gave 42.2% Co and 25.6% Zn.

Comparative Example A: Co₃O₄

In a 2 L Roto-Vap flask was mixed, 436.6 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1000 mL H_2O . After water removal, the sample was melted out of the flask, poured into a crystallizing dish and calcined in air at 400°C for two hours. Powder X-ray diffraction showed the presence of Co_3O_4 . Chemical analysis by inductively coupled plasma spectrometry gave 67.6% Co.

Comparative Example B: CoO

A sample of Cobalt(II) oxide was obtained from Alfa (lot number 100377) and granulated to -20/+40 mesh. Powder X-ray diffraction analysis showed the presence of CoO.

Test Procedure for Examples 1-15 and Comparative Examples A and B:

The catalysts were evaluated in a laboratory scale short contact time reactor, a 25 cm long x 4 mm i.d. quartz tube reactor equipped with a co-axial quartz thermocouple well. The void space within the reactor was packed with quartz chips. The catalyst bed was positioned with quartz wool at about the mid-length of the reactor. The catalyst bed was heated with a 4 inch (10.2 cm) 600 watt band furnace at 90% electrical output. All runs were done at a CH₄:O₂ molar ratio of 2:1 and at a pressure of 5 psig (136 kPa). The reactor effluent was analyzed using a gas chromatograph equipped with a thermal conductivity detector. The C, H and O mass balance were all between 98% and 102%. The runs were conducted over two operating days with 6 hours of run time each day. The comparative results of these runs are shown in Table 1, wherein gas hourly space velocity is indicated by "GHSV." As shown in Table 1, no evidence of catalyst deactivation occurred after 12 hours.

Table 1

Ex.	Vol (mL)	Wt. (g)	Temp (°C)	GHSV x10 ⁴	%CH ₄ /O ₂ Conv.	%CO/H ₂ Sel.	H ₂ :CO Ratio
1	1.2	0.9611	806	10.2	96/100	98/97	1.98
2	2.0	0.9013	780	6.1	95/100	98/97	1.98
3	2.0	1.1711	735	6.1	94/100	99/99	2.00
4	1.5	1.9275	670	8.1	93/100	97/97	2.00
5	2.0	1.2364	791	6.1	93/100	97/97	2.00
6	0.4	0.6065	782	30.4	90/100	95/95	2.00
7	1.4	1.1901	806	8.7	89/100	95/93	1.96
8	2.0	2.7610	782	6.1	89/100	95/93	1.96
9	2.0	2.5467	798	6.1	86/100	94/94	2.00
10	0.8	1.0675	750	15.2	85/100	93/88	1.89
11	0.7	0.9994	583	6.1	85/100	97/93	1.92
12	1.6	1.9054	750	7.6	83/100	92/91	1.98
13	2.0	2.1324	750	6.1	81/100	93/92	1.98
14	1.7	1.2404	641	7.2	81/100	93/90	1.94
15	1.6	2.3868	755	7.6	78/100	91/89	1.96
A	1.0	0.9820	939	12.2	52/100	81/58	1.43
B	1.1	2.1458	774	11.0	32/76	63/44	1.40

Feed: 30% CH₄, 15% O₂, 55% N₂

Comparative Examples A and B serve as comparative examples demonstrating that the Co oxides, themselves, are not as effective in catalyzing the partial oxidation of methane to syngas. As the data entries in Table 1 indicate, methane conversion and syngas selectivity are significantly lower for those runs which were catalyzed by Co₃O₄ and CoO.

Example 18: 12%(Co/Al/O)/PSZ

The powder catalyst prepared in Example 3 was first ground to less than 325 mesh, then 1.3909g of H₂O was added to the powder (0.3173g) in a glass vial to form a slurry. A PSZ foam (12mm OD x 10mm of 80ppi) from Vesuvius Hi-Tech Inc. was dipped into the slurry and saturated for 5 minutes. The foam was removed from the vial and the slurry remained in the pores of the foam was removed by blowing some compressed air. Finally, the foam was dried at 100°C for 2 hours.

Example 19: 9% (Co/Mg/O)/PSZ

The powder catalyst prepared in Example 4 was first ground to less than 325 mesh, then 1.2370g of H₂O was added to the powder (0.3067g) in a glass vial to form a slurry. A PSZ foam (12mm OD x 10mm of 80ppi) from Vesuvius Hi-Tech Inc. was dipped into the slurry and saturated for 5 minutes. The foam was removed from the vial and the slurry remained in the pores of the foam was removed by blowing some compressed air. Finally, the foam was dried at 100°C for 2 hours

Example 20: 12%(Co/Al/O), 4%MgO/PSZ

A PSZ foam (12mm OD x 10mm of 80ppi) from Vesuvius Hi-Tech Inc. was coated with 4 wt.% MgO by dripping a solution of Mg(NO₃)₂ 6H₂O (0.40g) in H₂O (1.25g) to saturation, evaporating off the solvent at room temperature, drying at 110°C overnight and calcining at 900°C for 2 hours.

The powder catalyst prepared in Example 3 was first ground to less than 325 mesh, then 1.3026g of H₂O was added to the powder (0.2965g) in a glass vial to form a slurry. The MgO coated PSZ foam was dipped into the slurry and saturated for 5 minutes. The foam was removed from the vial and the slurry remained in the pores of the foam was removed by blowing some compressed air. Finally, the foam was dried at 100°C for 2 hours.

Example 21: 14%(Co-Al-Substituted hydrotalcite) /PSZ

The powder catalyst prepared in Example 5 was first ground to less than 325 mesh, then 1.2271g of H₂O was added to the powder (0.2800g) in a glass vial to form a slurry. A PSZ foam (12mm OD x 10mm of 80ppi) from Vesuvius Hi-Tech Inc. was dipped into the slurry and saturated for 5 minutes. The foam was removed from the vial and the slurry remained in the pores of the foam was removed by blowing some compressed air. Finally, the foam was dried at 100°C for 2 hours.

Test Procedure for Examples 18-21

The partial oxidation reactions were done with a conventional flow apparatus using a 19 mm O.D. x 13 mm I.D. and 12" long quartz reactor. A ceramic foam of 99% Al₂O₃ (12 mm OD x 5 mm of 45 ppi) were placed before and after the catalyst as radiation shields. The inlet radiation shield also aided in uniform distribution of the feed gases. An Inconel sheathed, single point K-type (Chromel/Alumel) thermocouple (TC) was placed axially inside the reactor touching the top (inlet) face of the radiation shield. A high temperature S-Type (Pt/Pt 10% Rh) bare-wire TC was positioned axially touching the bottom face of the catalyst and was used to indicate the reaction temperature. The catalyst and the two radiation shields were sealed tight against the walls of the quartz reactor by wrapping them radially with a high purity (99.5%) alumina paper. A 600 watt band heater set at 90% electrical output was placed around the quartz tube, providing heat to light off the reaction and to preheat the feed gases. The bottom of the band heater corresponded to the top of the upper radiation shield. In addition to the TCs placed above and below the catalyst, the reactor also contained two axially positioned, triple-point TCs, one before and another after the catalyst. These triple-point thermocouples were used to determine the temperature profiles of reactants and products subjected to preheating and quenching, respectively. All runs were done at a CH₄:O₂ molar ratio of 2:1 with a combined flow rate of 2.5 standard liters per minute (SLPM) or 134,000/h gas hourly space velocity (GHSV) and at a pressure of 5 psig (136 kPa). The reactor effluent was analyzed using a gas chromatograph equipped with a thermal conductivity detector. The C, H and O mass balance were all between 98% and 102%.

TABLE 2**Syngas Production by Cobalt-based Catalysts**

Ex.	Preheat Temp. °C	Catal. Temp. °C	% CH ₄ / % O ₂ Conv.	% CO / % H ₂ Sel.	H ₂ :CO
18	509	814	82/99	96/93	1.94
19	505	913	80/100	96/92	1.92
20	499	885	86/100	97/96	1.98
21	507	851	89/100	97/94	1.94

Example 22. Co-MgO/PSZ

A Co-MgO solid solution catalyst supported on PSZ was prepared according to the following procedure (amounts given are for laboratory-scale batches): 4.3024 grams of
5 Mg(NO₃)₂·6H₂O (Aldrich 23,717-5) was dissolved in 4.1652 grams of distilled and de-ionized (DDI) water at about 50°C. This solution was added to a PSZ foam 12-mm diameter x 10-mm long, weighing 1.9245 grams. The wet PSZ foam was dried at about 70°C and calcined in air according to the following schedule: 10°C/min ramp up to 500°C; hold at 500°C for 2 hours; 10°C/min ramp down to room temperature. The above procedure was
10 repeated until 13 wt% MgO, based on the weight of PSZ foam, was obtained. 0.75 gram of Co(NO₃)₂·6H₂O (Aldrich 23,926-7) was dissolved in 1.86 grams of DDI water at about 50°C and added to the MgO-coated PSZ foam at about 70°C. The wet MgO-loaded PSZ foam was dried at about 70°C and calcined in air according to the following schedule: 5°C/min ramp up to 200°C; hold at 200°C for 1 hour; 5°C/min ramp up to 400°C; hold at 400°C for 1 hour;
15 5°C/min ramp up to 800°C; hold at 800°C for 12 hours; 10°C/min ramp down to room temperature. The resulting material contained a Co oxide loading of 0.1684 gram or 8.75 wt% based on the weight of PSZ foam. The catalyst was reduced with H₂ using 1:1 by volume flow of N₂:H₂ mixture at 0.3 standard liter per minute (SLPM) measured at 0°C and 1 atm pressure, using the following schedule: 5°C/min ramp up to 125°C; hold at 125°C for 0.5
20 hour; 5°C/min ramp up to 500°C; hold at 500°C for 3 hours; 5°C/min ramp down to room temperature. This catalyst had an estimated loading of 0.0687 g. Mg and 0.0626 g. Co based on the respective oxide weights. Calculated as metal wt% based on the final catalyst weight, the final catalyst had 5.7 wt% Co, 6.4 wt% Mg.

25 Example 23. (Pt/Co/MgO)/PSZ

A Co-MgO solid solution catalyst supported on PSZ was prepared according to the following procedure (amounts given are for laboratory-scale batches): 6.0664 grams of
Mg(NO₃)₂·6H₂O (Aldrich 23,717-5) was dissolved in 5.2249 grams of distilled and de-ionized (DDI) water at about 50°C. One-third of this solution was added to a PSZ foam 12-
30 mm diameter x 10-mm long, weighing 0.8628 gram. The wet PSZ foam was dried at about 70°C and calcined in air according to the following schedule: 5°C/min ramp up to 500°C; hold at 500°C for 2 hours; 10°C/min ramp down to room temperature. The above procedure

resulted in 12.33 wt% MgO, based on the weight of PSZ foam. 0.66 gram of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich 23,926-7) was dissolved in 1.5 grams of DDI water at about 50°C and added to the MgO-coated PSZ foam at about 70°C. The wet MgO-loaded PSZ foam was dried at about 70°C and calcined in air according to the following schedule: 5°C/min. ramp up to 200°C; 5 hold at 200°C for 1 hr.; 5°C/min. ramp up to 400°C; hold at 400°C for 1 hr.; 5°C/min. ramp up to 800°C; hold at 800°C for 12 hrs.; 10°C/min. ramp down to room temperature. . The above procedure resulted in 0.0876 gram or 11.15 wt% CoO, based on the weight of PSZ foam.. Addition of platinum was done as follows: 0.16 g. $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (Aldrich 27,872-6) was dissolved in 0.3 g. of distilled and deionized (DDI) water at about 70°C and added to 10 the CoO-MgO-coated PSZ foam, also at about 70°C. The wet foam was dried at about 70°C on a hotplate for about 2 hrs. and then calcined in air according to the following schedule: 5°C/min. ramp up to 110°C; hold at 125°C for 1/2 hr.; 5°C/min. ramp up to 250°C; hold at 250°C for 2 hr.; 10°C/min. ramp down to room temperature. The resulting material contained a Pt oxide loading of 0.0022 g., corresponding to a loading of 0.25% based on the 15 weight of PSZ foam. Based on the total weight of the catalyst after calcination, the composition was: 0.15% Pt, 6.5 % Co and 6.1% Mg. The catalyst was reduced with H_2 using a 1:1 (by volume) flow of $\text{N}_2:\text{H}_2$ mixture at 0.2 standard liters per minute (SLPM) measured at 0°C and 1 atm pressure, using the following schedule: 3°C/min. ramp up to 125°C; hold at 125°C for 0.5 hr; 3°C/min. ramp up to 500°C; hold at 500°C for 3 hrs; 20 5°C/min. ramp down to room temperature. Other promoters including Ni, Mn, La, Cu, Sm, Yb, Eu, Pr, Ce, Y, Rh, and Re may be substituted for Pt in the procedure to provide additional active syngas catalysts. These catalysts are made as described above, but substituting the corresponding metal salt solution for the $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ solution. Other refractory catalyst support materials may be substituted for PSZ, such as cordierite honeycomb or alpha-alumina 25 foam having about 40-400 pores per inch (ppi) density.

Test Procedure for Examples 22-23

Preferred syngas catalysts comprise catalytically active cobalt-containing components supported on a ceramic monolith porous carrier such as partially stabilized zirconia (PSZ) 30 foam (stabilized with Mg, Y or Ca). PSZ foams have been described in the literature (e.g., U.S. Patent No. 4,835,123 (Bush et al.)) and are commercially available from suppliers such as Vesuvius Hi-Tech Ceramics Inc., Alfred Station, New York. Alternatively the catalyst support may be α -alumina foam (also stabilized with Zr) or "honeycomb" straight channel

extrudate made of cordierite or mullite. In the present series of tests, the catalyst support was a laboratory-scale ceramic monolith comprising porous PSZ foam with approximately 6,400 channels per square inch (80 pores per linear inch). The monolith was cylindrical overall, with a diameter corresponding to the inside diameter of the reactor tube and the length
5 varying from 1/8" to 1-1/2". These catalysts were tested substantially as described in the section entitled Test Procedure for Examples 18-21, using a feed containing natural gas or methane and oxygen in the molar ratio of from 1.7:1 to 2.3:1 ($\text{CH}_4:\text{O}_2$ ratio) at a total GHSV of from 61,000 1/h to 1,000,000 1/h in the laboratory-scale reactor (at 5-15 psig) and pilot unit (at 15-400 psig) testing. The laboratory-scale tests used methane and oxygen feed, while
10 the pilot unit tests used natural gas and oxygen feed. Reacted gases were analyzed for content of CH_4 , O_2 , CO , H_2 , CO_2 , and, optionally, other components. The results of those tests are shown in Table 3.

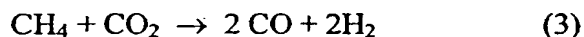
Table 3

Performance of Co-MgO Supported on PSZ foam

Example	Composition	CH ₄ :O ₂ molar feed ratio	Combined Flowrate in GHSV	Pressure	Preheat Temp.	Catalyst Temp.	%CH ₄ /%O ₂ Conv.	%CO/%H ₂ Sel.	H ₂ :CO
22	5.7 wt% Co, 6.3 wt% Mg	1.75	192,300	5 psig	150°C	840°C	93/100	96/90	1.7
22	5.7 wt% Co, 6.3 wt% Mg	1.75	391,200	7 psig	150°C	910°C	85/100	96/84	1.6
23	0.15 wt% Pt, 6.5 wt% Co, 6.1 wt% Mg	2.00	1,300,000	45 psig	488°C	1094°C	81/100	93/67	1.7

Compared to the performance of the catalyst of Example 19, it can be seen that an unpromoted Co-MgO catalyst prepared by the multi-step loading procedure and having a composition as in Example 22 resulted in higher levels of CH₄ conversion and selectivity for CO and H₂ products operating at higher space velocities than in Example 19. Inclusion of very small amounts of Pt in the catalyst, prepared as described in Example 23, has the effect of lowering the light off temperature while not increasing the reaction temperature, at pressures as high as 45 psig and flow rates as high as 1.3 million GHSV. In addition, this catalyst showed excellent resistance to coking and Co metal loss by volatilization over 9 days, normally observed with unpromoted Co-based catalysts at higher flowrates.

Excellent levels of conversion of methane and oxygen reactants and selectivities for CO and H₂ products by a predominantly, or net catalytic partial oxidation reaction are achievable by the new catalyst devices in a short contact time reactor. The term "net catalytic partial oxidation" means that the partial oxidation reaction of Equation 2 predominates over reforming reactions, and the molar ratio of the H₂:CO products is preferably about 2:1. Although not wishing to be bound by a particular theory, the inventors believe that the primary reaction catalyzed by the preferred catalysts described herein is the partial oxidation reaction of Equation 2. Other chemical reactions may also occur, but to a lesser extent, catalyzed by the same catalyst device, to yield an overall or net partial oxidation reaction. For example, in the course of syngas generation, intermediates such as CO₂ + H₂O may occur as a result of the oxidation of methane, followed by a reforming step to produce CO and H₂. Also, particularly in the presence of carbon dioxide-containing feedstock or CO₂ intermediate, the reaction shown in Equation 3



may also occur to some extent during the production of syngas, in which case the molar ratio of the H₂ and CO products is somewhat less than the preferred Fischer-Tropsch stoichiometric molar ratio of 2:1 H₂:CO.

Process for Producing Syngas

The reactants are contacted with the catalyst in a fixed bed configuration in the reaction zone of a millisecond contact time reactor. Particles of the catalyst or supported catalyst are retained in the reaction zone using fixed bed techniques well known in the art. Alternatively, a catalyst device, or impregnated monolith, prepared as described above, is employed. The catalyst or catalyst device preferably has sufficient permeability or porosity

to permit a stream of said reactant gas mixture to pass over it at a gas hourly space velocity of at least about 20,000 NL/kg/hr, when the reactor is operated to produce synthesis gas.

A feed stream comprising a hydrocarbon feedstock and an oxygen-containing gas is contacted with one of the above-described catalysts comprised of cobalt metal and/or cobalt containing compound(s) in a reaction zone maintained at conversion-promoting conditions effective to produce an effluent stream comprising carbon monoxide and hydrogen. The hydrocarbon feedstock is any gaseous hydrocarbon having a low boiling point, such as methane, natural gas, associated gas, or other sources of light hydrocarbons having from 1 to 5 carbon atoms. For example, the hydrocarbon feedstock may be a gas arising from naturally occurring reserves of methane, and may also contain carbon dioxide. Preferably, the feed comprises at least 50% by volume methane, more preferably at least 75% by volume, and most preferably at least 80% by volume methane. The hydrocarbon feedstock is in the gaseous phase when contacting the catalyst. The hydrocarbon feedstock is contacted with the catalyst as a mixture with an oxygen-containing gas, preferably pure oxygen. The oxygen-containing gas may also comprise steam and/or CO₂ in addition to oxygen. Alternatively, the hydrocarbon feedstock is contacted with the catalyst as a mixture with a gas comprising steam and/or CO₂.

The preheated feed gases pass over or through the monolith or catalyst device to heat the catalytic materials to the point at which they ignite and start the reaction. A net partial oxidation reaction ensues, and the reaction conditions are maintained to promote continuation of the autothermal process. For the purposes of this disclosure, "autothermal" means that after catalyst ignition, no additional heat is supplied to the catalyst in order for the production of synthesis gas to continue. Autothermal reaction conditions are promoted by optimizing the concentrations of hydrocarbon and O₂ in the reactant gas mixture. Preferably the methane-containing feed and the oxygen-containing gas are mixed in such amounts to give a carbon to oxygen (i.e., O₂) molar ratio from about 1.25:1 to about 3.3:1, more preferably, from about 1.3:1 to about 2.2:1, and most preferably from about 1.5:1 to about 2.2:1, especially the stoichiometric ratio of 2:1. The hydrocarbon:oxygen (i.e., O₂) molar ratio of the reactant gas mixture is an important variable for maintaining the partial oxidation reaction and the desired product selectivities. Residence time, amount of feed preheat and amount of nitrogen dilution, if used, also affect the selectivity and yield of reaction products. The dwell time or residence time of the portion of gas mixture in contact with the catalyst is preferably maintained at no more than about 10 milliseconds.

This ultra short contact time is accomplished by passing the reactant gas mixture over or through one or more of the above-described cobalt-containing catalyst devices at a space velocity of about 20,000 to about 100,000,000 normal liters of gas per kilogram of catalyst per hour (NL/kg/h). Preferably the space velocity is about 50,000 to about 50,000,000 NL/kg/h. The process is operated at atmospheric or superatmospheric pressures, the latter being preferred. The pressures may be from about 100 kPa to about 12,500 kPa, preferably from about 130 kPa to about 10,000 kPa. The process is preferably operated at temperatures of from about 60°C to about 1,200°C, preferably from about 700°C to about 1,100°C. The hydrocarbon feedstock and the oxygen-containing gas are preferably pre-heated at about 60°C - 700°C, preferably from about 100°C to about 500°C, before contact with the catalyst. The hydrocarbon feedstock and the oxygen-containing gas are passed over the catalyst at any of a variety of space velocities. The product gas mixture emerging from the reactor is collected and may be routed to a syngas-consuming process such as a Fischer-Tropsch operation.

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. The disclosure of U.S. Provisional Patent Application No. 60/165,981 filed November 17, 1999 and all patents and publications cited herein are incorporated by reference.

CLAIMS

What is claimed is:

- 5 1. A syngas catalyst device comprising cobalt metal and/or at least one oxidizable cobalt containing compound and a support structure comprising a substance chosen from the group consisting of hydrotalcites, spinels, perovskites, magnesium oxide, pyrochlores, brownmillerites, zirconium phosphate, magnesium stabilized zirconia, zirconia stabilized alumina, silicon carbide, yttrium stabilized zirconia, calcium stabilized zirconia, yttrium
10 aluminum garnet, alumina, lanthanum oxide, cordierite, mullite, LaZrO_2 , ZrO_2 , ZnO , LaAlO_3 , MgAl_2O_4 , SiO_2 and TiO_2 .
2. The catalyst device of claim 1 comprising cobalt metal and/or said at least one cobalt containing compound disposed on said support structure.
3. The catalyst device of claim 1 wherein said support structure comprises a substance
15 chosen from the group consisting of hydrotalcites, spinels, perovskites, magnesia, LaZrO_2 , Al_2O_3 , and lanthanum oxide, and said cobalt metal and/or said at least one cobalt containing compound is incorporated into said support structure.
4. The catalyst device of claim 1 wherein said substance comprises at least one refractory metal oxide.
- 20 5. The catalyst device of claim 1 wherein said support structure comprises a refractory ceramic foam.
6. The catalyst device of claim 5 wherein said foam structure comprises about 12-60 pores per centimeter of structure.
7. The catalyst device of claim 4 wherein said support structure comprises a honeycomb
25 monolith structure.
8. The catalyst device of claim 1 wherein said cobalt metal and/or said at least one cobalt containing compound comprises a mixture of cobalt metal and a metal oxide chosen from the group consisting of cobalt oxide and magnesium oxide, in the form of a solid solution.
- 30 9. The catalyst device of claim 1 comprising a spinel chosen from the group consisting of MgCo_2O_4 and Mg_2CoO_4 .
10. The catalyst device of claim 1 comprising a spinel-like formation chosen from the group consisting of:

Co/Mg/O and MgO ,

Co/Mg/O,
Co/Al/O and Al₂O₃, and
Co/Al/O.

11. The catalyst device of claim 1 comprising a compound chosen from the group
5 consisting of CoAl₂O₄ and Co₂AlO₄.
12. The catalyst device of claim 1 comprising a mixture of cobalt metal and/or cobalt
oxide and Al₂O₃.
13. The catalyst device of claim 1 comprising a cobalt-containing hydrotalcite.
14. The catalyst device of claim 1 comprising a cobalt hydrotalcite having the formula
10 Co₆Al₂(OH)₁₆CO₃ • 4 H₂O.
15. The catalyst device of claim 1 comprising cobalt metal and/or cobalt oxide supported
on LaZrO₂.
16. The catalyst device of claim 1 comprising cobalt metal and/or cobalt oxide supported
on lanthanum oxide doped zirconia.
- 15 17. The catalyst device of claim 1 comprising LaAl₈Co₂O₃.
18. The catalyst device of claim 1 comprising a mixture of the metals and/or metal oxides
of La, Al and Co.
19. The catalyst device of claim 1 comprising cobalt metal and/or cobalt oxide supported
on a mixture of alumina and lanthanum oxide.
- 20 20. The catalyst device of claim 1 comprising a compound chosen from the group
consisting of CaCo₂O₄ and Ca₂CoO₄.
21. The catalyst device of claim 1 comprising a mixed metal oxide chosen from the group
consisting of:
- 25 Co/Ca/O, and
Co/Ca/O and CaO.
22. The catalyst device of claim 1 comprising Co metal and/or cobalt oxide supported on
CaO.
23. The catalyst device of claim 1 comprising a compound chosen from the group
consisting of ZnCo₂O₄ and Zn₂CoO₄.
- 30 24. The catalyst device of claim 1 comprising a mixed metal oxide chosen from the group
consisting of:
- Zn/Co/O and ZnO, and
Zn/Co/O.

25. The catalyst device of claim 1 comprising cobalt metal and/or cobalt oxide supported on ZnO.
26. The catalyst device of claim 1 comprising a mixed metal oxide of Co/Ni/Na/Al/O.
27. The catalyst device of claim 1 comprising a mixture of metals and/or metal oxides
5 chosen from the group consisting of Co, Ni, Na and Al, and oxides thereof.
28. A syngas catalyst device comprising cobalt metal and/or cobalt oxide, a promoter chosen from the group consisting of Mn, Ni, La, Cu, Sm, Yb, Eu, Pr, Ce, Y, Pt, Rh and Re, and a support structure chosen from the group consisting of alumina and partially stabilized zirconia.
- 10 29. The catalyst device of claim 28 comprising cobalt metal and/or cobalt oxide, magnesium oxide, platinum metal and/or platinum oxide and a partially stabilized zirconia support.
30. The catalyst device of claim 29 comprising about 0.15% Pt, about 6.5% Co and about 6.1% Mg.
- 15 31. A syngas catalyst prepared by
impregnating a refractory metal oxide support with a solution of an oxidizable magnesium salt;
calcining said magnesium impregnated support;
impregnating said magnesium impregnated support with a solution of an oxidizable
20 cobalt salt to provide a cobalt/magnesium oxide intermediate;
calcining said cobalt/magnesium oxide intermediate;
impregnating said cobalt/magnesium intermediate with a solution of an oxidizable promoter salt, said promoter chosen from the group of metals consisting of Mn, Ni, La, Cu, Sm, Yb, Eu, Pr, Ce, Y, Pt, Rh and Re, to provide a promoter/cobalt/magnesium oxide
25 intermediate;
calcining said promoter/cobalt/magnesium oxide intermediate; and
reducing said calcined promoter/cobalt/magnesium oxide intermediate to provide a supported catalyst having activity for catalyzing the net partial oxidation of methane in the presence of O₂ to CO and H₂ under reaction promoting conditions in a short contact time
30 reactor.
32. A method of producing synthesis gas comprising:
in a millisecond contact time reactor, passing a reactant gas mixture comprising a C₁-C₅ hydrocarbon and an O₂-containing gas over the catalyst device of claim 1, such that the

contact time of a portion of said reactant gas mixture in contact with said catalyst device does not exceed about 10 milliseconds;

maintaining net catalytic partial oxidation promoting conditions of hydrocarbon:O₂ molar ratio in said reactant gas mixture, catalyst temperature and reactant gas preheat temperature.

33. The method of claim 32 wherein said step of maintaining said net catalytic partial oxidation promoting conditions includes maintaining a catalyst temperature of about 600-1,200°C.

34. The method of claim 32 further comprising mixing a methane-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock having a hydrocarbon:O₂ molar ratio of about 1.25:1 to about 3.3:1.

35. The method of claim 34 wherein said mixing provides a reactant gas mixture feed having a hydrocarbon:O₂ molar ratio of about 1.5:1 to about 2.2:1.

36. The method of claim 35 wherein said mixing provides a reactant gas mixture feed having a carbon:oxygen ratio of about 2:1.

37. The method of claim 32 wherein said O₂-containing gas further comprises steam, CO₂, or both.

38. The method of claim 32 further comprising mixing a hydrocarbon feedstock and a gas comprising steam and/or CO₂ to provide said reactant gas mixture.

39. The method of claim 32 wherein said C₁-C₅ hydrocarbon comprises at least about 50 % methane by volume.

40. The method of claim 32 further comprising preheating said reactant gas mixture.

41. The method of claim 32 wherein said step of passing said reactant gas mixture over said catalyst device comprises passing said reactant gas mixture over said catalyst device at a space velocity of about 20,000 to about 100,000,000 normal liters of gas per kilogram of catalyst per hour (NL/kg/h).

42. A method of producing synthesis gas comprising:

in a millisecond contact time reactor, passing a reactant gas mixture comprising a C₁-C₅ hydrocarbon and an O₂-containing gas over the catalyst device of claim 28, such that the contact time of a portion of said reactant gas mixture in contact with said catalyst device does not exceed about 10 milliseconds;

maintaining net catalytic partial oxidation promoting conditions of hydrocarbon:O₂ molar ratio in said reactant gas mixture, catalyst temperature and reactant gas preheat temperature.

43. The method of claim 42 wherein said step of maintaining said reaction promoting conditions includes maintaining a catalyst temperature of about 600-1,200°C.

44. The method of claim 42 wherein said step of maintaining net catalytic partial oxidation promoting conditions comprises mixing a methane-containing feedstock and an O₂-
5 containing feedstock to provide a reactant gas mixture having a hydrocarbon:O₂ molar ratio of about 1.25:1 to about 3.3:1.

45. The method of claim 44 wherein said mixing provides a reactant gas mixture feed having a hydrocarbon:O₂ molar ratio of about 1.5:1 to about 2.2:1.

46. The method of claim 45 wherein said mixing provides a reactant gas mixture feed
10 having a hydrocarbon:O₂ molar ratio of about 2:1.

47. The method of claim 41 wherein said O₂-containing gas further comprises steam, CO₂, or both.

48. The method of claim 41 further comprising mixing a hydrocarbon feedstock and a gas comprising steam and/or CO₂ to provide said reactant gas mixture.

49. The method of claim 41 wherein said C₁-C₅ hydrocarbon comprises at least about 50
15 % methane by volume.

50. The method of claim 41 further comprising preheating said reactant gas mixture.

51. The method of claim 41 wherein said step of passing said reactant gas mixture over said catalyst device comprises passing said reactant gas mixture over said catalyst device at a
20 space velocity of about 20,000 to about 100,000,000 normal liters of gas per kilogram of catalyst per hour (NL/kg/h).

52. A method of converting a C₁-C₅ hydrocarbon comprising at least about 50 vol% methane to a product gas mixture comprising CO and H₂, the process comprising:

mixing a methane-containing feedstock and an O₂-containing feedstock to provide a
25 reactant gas mixture having a hydrocarbon:O₂ ratio of about 1.25:1 to about 3.3:1;

passing said reactant gas mixture over a catalyst device comprising

cobalt metal and/or cobalt oxide,

optionally, a promoter chosen from the group consisting of Mn, Ni, La, Cu, Sm, Yb, Eu, Pr, Ce, Y, Pt, Rh, and Re, and

30 a catalyst support structure comprising a substance chosen from the group consisting of partially stabilized zirconia, hydrotalcites, spinels, perovskites, magnesia, LaZrO₂, alumina, and lanthanum oxide;

passing said reactant gas mixture feedstock over said catalyst at a space velocity of about 20,000 to about 100,000,000 normal liters of gas per kilogram of catalyst

per hour (NL/kg/h), such that the contact time of a portion of said reactant gas mixture in contact with said catalyst device is no more than about 10 milliseconds;

maintaining the temperature of said catalyst device at about 600-1,200°C; and,
optionally, preheating said reactant gas mixture.

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(54) Title: COBALT-BASED CATALYSTS AND PROCESS FOR PRODUCING SYNTHESIS GAS

(57) Abstract: A process is disclosed for the catalytic partial oxidation of light hydrocarbons such as methane. The process involves the conversion of a hydrocarbon feedstock by contacting a feed stream comprising the hydrocarbon feedstock and an oxygen-containing gas with a catalyst in a reaction zone maintained at conversion-promoting conditions in a millisecond contact time reactor effective to produce an effluent stream containing primarily carbon monoxide and hydrogen. Certain preferred catalysts of the invention comprise cobalt metal and/or cobalt containing compound(s), a promoter, and a refractory support are capable of efficiently producing syngas at high selectivities for CO and H₂ products.

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INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B3/40 C01B3/38 B01J23/75 B01J23/76 B01J23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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IPC 7 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

API Data, WPI Data, PAJ, INSPEC, COMPENDEX, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	M. P. MAKOA ET AL.: "Characterisation of Co/Mg/Al ₂ O ₃ high pressure partial oxidation catalysts" CATALYSIS TODAY, vol. 49, 24 February 1999 (1999-02-24), pages 11-16, XP002159880 the whole document	1-4,9,10,32-41,52
X	US 5 756 421 A (PRABHAKAR BATHULA ET AL) 26 May 1998 (1998-05-26) cited in the application examples 18-22	1-4,10,32-41,52
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 008, no. 052 (C-213), 9 March 1984 (1984-03-09) & JP 58 207946 A (TOYODA CHUO KENKYUSHO KK), 3 December 1983 (1983-12-03) abstract	1,2,4, 32-41,52
X	--- CHEMICAL ABSTRACTS, vol. 131, no. 10, 6 September 1999 (1999-09-06) Columbus, Ohio, US; abstract no. 135150, CIMINO, ALESSANDRO ET AL: "High and low surface area NiO-MgO and CoO-MgO solid solutions: a study of XPS surface composition and CO oxidation activity" XP002159881 abstract & TOP. CATAL. (1999), 8(3,4), 171-178, 1999,	1-8
X	--- CHEMICAL ABSTRACTS, vol. 129, no. 18, 2 November 1998 (1998-11-02) Columbus, Ohio, US; abstract no. 236141, KHASIN, A. A. ET AL: "Structural evolution of a Co-Mg oxide catalyst in hydrogen and carbon monoxide atmospheres: effect of the cobalt particle size on the structure of carbon formed in the reaction of CO disproportionation" XP002159882 abstract & KINET. CATAL. (1998), 39(3), 400-410, 1998,	1-8
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A	--- EP 0 656 317 A (SHELL INT RESEARCH) 7 June 1995 (1995-06-07) the whole document -----	1-10, 32-41,52

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/31451

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

claims 1-10 (in as far as they concern catalysts containing cobalt, magnesium and oxygen), 32-41, 52

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: Claims 1-10 (in as far as they concern catalysts containing cobalt, magnesium and oxygen), 32-41, 52

Catalysts suitable for the generation of synthesis gas comprising cobalt, magnesium and oxygen and process for generating synthesis gas using that catalyst.

2. Claims: Claims 1-7, 10 (in as far as these claims concern catalysts comprising cobalt, aluminium and oxygen), 11-14, 32-41, 52

Catalysts suitable for the generation of synthesis gas comprising cobalt, aluminium and oxygen and process for generating synthesis gas using that catalyst.

3. Claims: Claims 1-7 (in as far as these claims concern catalysts comprising cobalt, lanthanum and oxygen), 15-19, 32-41, 52

Catalysts suitable for the generation of synthesis gas comprising cobalt, lanthanum and oxygen and process for generating synthesis gas using that catalyst.

4. Claims: Claims 1-7 (in as far as these claims concern catalysts comprising cobalt, calcium and oxygen), 20-22, 32-41, 52

Catalysts suitable for the generation of synthesis gas comprising cobalt, calcium and oxygen and process for generating synthesis gas using that catalyst.

5. Claims: Claims 1-7 (in as far as these claims concern catalysts comprising cobalt, zinc and oxygen), 23-25, 32-41, 52

Catalysts suitable for the generation of synthesis gas comprising cobalt, zinc and oxygen and process for generating synthesis gas using that catalyst.

6. Claims: Claims 1-7 (in as far as these claims concern catalysts comprising cobalt, nickel,

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

sodium and oxygen), 26, 27, 32-41, 52

Catalysts suitable for the generation of synthesis gas comprising cobalt, nickel, sodium and oxygen and process for generating synthesis gas using that catalyst.

7. Claims: Claims 28-31, 42-51,
52 (as far as the optional promoters are present):

Catalysts suitable for the generation of synthesis gas, comprising cobalt and a promoter chosen from Mn, Ni, La, Cu, Sm, Yb, Eu, Pr, Ce, Y, Pt, Rh and a support chosen from alumina and partially stabilised zirconia and process for generating synthesis gas using that catalyst.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/31451

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